effect from a Debye-Waller factor and the opposing multiphonon processes. In addition to the effect of thermal expansion we find a non-linearity which, however, agrees both in sign and magnitude with the effect of purely anharmonic shifts in the phonon frequencies.

(iii) Finally we have reanalysed experiments on the volume dependence of the effective electron mass. In the literature on this subject it has not been recognized how large the electron-phonon enhancement of the mass is for lead. When we take this fact into account, we find that the band mass decreases when the lattice expands, instead of a supposed increase.

Appendix 1

We follow COWLEY and COWLEY [24] and write for the phonon frequency $\omega(q, \lambda)$ as measured e.g. with inelastic neutron scattering

$$\omega(q, \lambda) = \omega_0(q, \lambda) + \Delta_1(q, \lambda) + \Delta_2(q, \lambda) + \Delta_3(q, \lambda). \qquad (A1)$$

The three last terms represent anharmonic corrections. Δ_1 takes into account the effect of thermal expansion. Δ_2 and Δ_3 represent purely anharmonic effects, they originate from the third and fourth order derivatives of the effective interatomic potential. At high temperatures Δ_2 and Δ_3 are linear in T and they are also volume dependent. The standard Grüneisen γ_G can be expressed in the isothermal compressibility K_T and the thermal expansion coefficient β, but also as a derivative of the entropy

$$\gamma_G = \frac{\beta V}{C_v K_T} = \frac{V}{C_v} \left(\frac{\partial S}{\partial V} \right)_T. \qquad (A2)$$

COWLEY and COWLEY find for the volume dependent part ΔS of the entropy

$$\Delta S = - \hbar \sum_{\lambda, q} \frac{\partial}{\partial T} \left[\frac{1}{e^{\hbar \omega(q, \lambda)/kT} - 1} \right] [\Delta_1(q, \lambda) + \Delta_2(q, \lambda) + \Delta_3(q, \lambda)]. \qquad (A3)$$

Therefore the high temperature γ_G measures the average of the relative volume dependence of the phonon frequencies

$$\gamma_G \approx \frac{1}{3N} \sum_{i=1}^{3N} (d \ln \omega_i / d \ln V)_T. \qquad (A4)$$

The result above is valid when $T \gtrsim \Theta_D$, but it only represents the lowest correction and must not be used at higher temperatures where the frequency shifts are more complicated and the frequencies less well defined because of damping effects. Experiments on lead by LEADBETTER [19] suggest that the range of validity for lead is $\Theta_D \lesssim T \lesssim 3\Theta_D (\Theta_D \approx 90\,°K)$. From the measurements of LEADBETTER we find $\gamma_G(270\,°K) = 2.7$ and we use this value for $(d \ln \Theta_R / d \ln V)_T$. (cf. appendix 2) $(d \ln \Theta_\lambda / d \ln V)_T$ refers to very low temperatures but the weighting of different modes is the same as for the high temperature γ_G. At low temperatures Δ_2 and Δ_3 are small (although not zero). This fact leads us to consider γ_G calculated without the terms Δ_2 and Δ_3, and at crystal volume $V_0 = V(T = 0)$. Leadbetter gives the value 2.7 for this quantity and we thus have $(d \ln \Theta_\lambda / d \ln V) = 2.7$ (cf. Appendix 2).

Appendix 2

From tunneling experiments in superconductors one can obtain a quantity $\alpha^2(\omega) F(\omega)$ [6], giving the product of the strength of electron-phonon interaction $\alpha^2(\omega)$ as a function of energy, and the phonon density of states $F(\omega)$. Using this function, it is possible to rewrite Eq. 1 for the electrical resistivity in the form [3]

$$\varrho = \left(\frac{S}{S_0} \right)^2 \frac{N_{bs}(0)}{N_{fe}(0)} \frac{4 \pi m \hbar \overline{(1 - \cos \Theta)}}{n e^2 k T} \int \frac{\alpha^2(\omega) F(\omega) \omega \, d\omega}{[e^{\hbar \omega/kT} - 1][1 - e^{-\hbar \omega/kT}]} \qquad (A5)$$

where S/S_0 is the ratio between the true free area of the Fermi surface and the area in the free electron case. $N_{bs}(0)/N_{fe}(0)$ is the corresponding ratio for the density of electron states at the Fermi level. $\overline{1 - \cos \Theta}$ denotes the average of the usual factor $1 - \cos \Theta$ that enters expressions for the resistivity. This factor has been rewritten in Eq. 1, using $q^2 = 2 k_F (1 - \cos \Theta)$. Let us now make the assumption that $1 - \cos \Theta$ is approximately the same if it is considered separately for transverse phonons and for longitudinal phonons. In a polyvalent metal, where the resistivity is totally dominated by Umklapp scattering, this should be a reasonable approximation. We then take the high temperature limit of Eq. A1 and find that the relative importance of phonons of energy ω in the resistivity is given by $\alpha^2(\omega) F(\omega)/\omega$.

In the high temperature Grüneisen γ_G, all individual $\gamma(q, \lambda)$ are equally weighted

$$\gamma_G = \int F(\omega) \overline{\gamma}(\omega) d\omega = \frac{2}{3} \overline{\gamma}_T + \frac{1}{3} \overline{\gamma}_L \qquad (A6)$$

where $\overline{\gamma}(\omega)$ is an average over all individual phonon modes with energy in $[\omega, \omega + d\omega]$. $\overline{\gamma}_T$ and $\overline{\gamma}_L$ are averages for the transverse and longitudinal branches. For $\gamma_R = (d \ln \Theta_R / d \ln V)$ we could write

$$\gamma_R \approx \int \frac{\alpha^2(\omega) F(\omega)}{\omega} \overline{\gamma}(\omega) d\omega. \qquad (A7)$$

The function $\alpha^2(\omega) F(\omega)$ has been obtained by McMILLAN and ROWELL [6]. It turns out that $\alpha^2(\omega)/\omega$ does not vary very much with ω in the region of typical phonon energies. From a study of the experimentally determined $\alpha^2(\omega) F(\omega)/\omega$ we have found it reasonable to take

$$\gamma_R = \frac{3}{4} \overline{\gamma}_T + \frac{1}{4} \overline{\gamma}_L. \qquad (A8)$$

The individual $\gamma(q, \lambda)$ can vary very much with q, but the general behaviour is the same for the transverse and the longitudinal branches (Fig. 1). Therefore γ_G should not be too bad as an approximation for γ_R.

If we make a series expansion in the denominator of Eq. 1, the first non-vanishing term gives a linear temperature dependence for the resistivity at high temperatures. The small correction for lead at room temperature from higher order terms can easily be estimated if we approximate $\alpha^2(\omega) F(\omega)/\omega$ by two sharp peaks at characteristic transverse and longitudinal frequencies and give them weights in the ratio 3: 1 (cf. Eq. A9). We finally turn to $(d \ln \Theta_\lambda / d \ln V)_P$. One has rigorously [6]

$$\lambda = 2 \int \frac{\alpha^2(\omega) F(\omega)}{\omega} d\omega. \qquad (A9)$$